

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
12 September 2002 (12.09.2002)

PCT

(10) International Publication Number  
WO 02/070452 A1

(51) International Patent Classification<sup>7</sup>: C07C 68/06,  
69/96, 31/20, 27/02

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(21) International Application Number: PCT/US01/07038

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(22) International Filing Date: 28 February 2001 (28.02.2001)

(81) Designated States (national): JP, KR.

(25) Filing Language: English

(84) Designated States (regional): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE, TR).

(26) Publication Language: English

Published:  
— with international search report

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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A1

(54) Title: PROCESS FOR CO-PRODUCTION OF DIALKYL CARBONATE AND ALKANEDIOL

WO 02/070452 A1  
(57) Abstract: A method is provided for co-producing dialkyl carbonate and alkanediol by reacting alkylene carbonate with alkanol in the presence of a IIIA metal oxide catalyst, preferably alumina.

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**PROCESS FOR CO-PRODUCTION OF  
DIALKYL CARBONATE AND ALKANEDIOL**

**BACKGROUND**

[0001] This invention relates to a method of co-producing dialkyl carbonate and alkanediol, and, in particular, to a method for enhancing the efficiency of the co-production by the use of a IIIA metal oxide catalyst containing hydroxyl groups.

[0002] Various homogeneous catalysts have been proposed for carbonate transesterification. For example, U.S. Pat. Nos. 3,642,858 and 4,181,676 disclose the preparation of dialkyl carbonates by transesterifying alkylene carbonates with alcohols in the presence of alkali metals or alkali metal compounds without the use of a support material. U.S. Pat. No. 4,661,609 teaches the use of a catalyst selected from the group consisting of zirconium, titanium and tin oxides, salts or complexes thereof.

[0003] Commercial use of homogeneous catalysts is restricted because separation of the catalyst from the unconverted reactants and organic product can be difficult. Because the transesterification is an equilibrium reaction, in an attempt to isolate the intended dialkyl carbonate by distillation of the reaction liquid without advance separation of the catalyst, the equilibrium is broken during the distillation and a reverse reaction is induced. Thus, the dialkyl carbonate once formed reverts to alkylene carbonate. Furthermore, due to the presence of the homogenous catalyst, side reactions such as decomposition, polymerization, or the like concurrently take place during the distillation which decrease the efficiency.

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[0004] Various heterogenous catalysts have also been proposed for carbonate transesterification. The use of alkaline earth metal halides is disclosed in U.S. Pat. No. 5,498,743. Knifton, et al., "Ethylene Glycol-Dimethyl Carbonate Cogeneration," *J. Molec. Catal.* 67:389-399 (1991) disclose the use of free organic phosphines or organic phosphines supported on partially cross-linked polystyrene. U.S. Pat. No. 4,691,041 discloses the use of organic ion exchange resins, alkali and alkaline earth silicates impregnated into silica, and certain ammonium exchanged zeolites. U.S. Pat. No. 5,430,170 discloses the use of a catalyst containing a rare earth metal oxide as the catalytically active component. The use of hydrotalcites is disclosed in Japanese Unexamined Patent Application 3[1991]-44,354. The use of MgO is disclosed in Japanese Unexamined Patent Application 6[1994]-107,601. The use of zeolites ion-exchanged with alkali metal and/or alkaline earth metal, thereby containing a stoichiometric amount of metal, are disclosed in U.S. Pat. No. 5,436,362.

[0005] Inorganic heterogenous catalysts generally possess thermal stability and easy regeneration. However, these catalysts, including the zeolites containing a stoichiometric amount of alkali or alkaline earth metal, generally demonstrate low activity and/or selectivity and are unsatisfactory for commercial application.

[0006] Polymer supported organic phosphines and ion exchange resins show high activity and good to excellent selectivity in transesterification reaction between alkylene carbonate and alkanol; however, these polymeric materials do not appear very stable and gradually lose catalytic activity, especially at relatively high temperatures.

[0007] Thus, there remains a need for a method of transesterifying alkylene carbonate with alkanol to co-produce dialkyl carbonate and alkanediol which

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will provide higher feed conversion and product selectivity over a wide temperature range.

### SUMMARY OF INVENTION

[0008] A method is provided for co-producing dialkyl carbonate and alkanediol by reacting alkylene carbonate with alkanol in the presence of a IIIA metal oxide catalyst. The preferred alkylene carbonate is ethylene carbonate and the preferred alkanol is methanol.

[0009] The preferred metal oxide of the catalyst is alumina. It is also preferred that the catalyst contain hydroxyl groups. The hydrated catalyst will usually contain hydroxyl groups in an amount greater than 0.1 wt% and less than 30 wt% of the catalyst. Another preferred embodiment includes the catalyst having an octahedral structure. The catalyst can further include an inert catalyst support.

[0010] The alumina catalyst is preferably prepared through dehydration of aluminum trihydroxide or aluminum monohydroxide, such as pseudoboehmite.

[0011] The process conditions include a reaction temperature of about 20°C (68°F) to about 300°C (572°F), a reaction pressure of about 14 to about 4000 psig, a liquid hour space velocity of about 0.1 to 40 hr<sup>-1</sup>, and a molar ratio of alkanol to alkylene carbonate of about 1-20.

[0012] Unlike polymer catalysts such as ion exchange resins, the IIIA metal oxide catalysts used in the method of the invention are thermally stable and regenerable. The combination of high catalytic activity and selectivity in a wide temperature range, and excellent thermal stability and regenerability of the

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catalysts, render them suitable for commercial use in co-producing organic carbonate and alkanediol through ester exchange reaction. Also, the general availability and low cost of alumina catalysts could significantly improve the process economics.

[0013] The organic carbonates produced by the method of the invention, dimethyl carbonate in particular, have potential application as "green" replacements for phosgene that is used mainly in manufacture of polyurethane and polycarbonate resins.

#### BRIEF DESCRIPTION OF DRAWINGS

[0014] Figure 1 is a graph demonstrating EC (ethylene carbonate) conversion vs. temperature for the MeOH/EC reaction using pseudoboehmite alumina,  $\gamma$ -alumina, and Cs-alumina as the catalysts.

[0015] Figure 2 is a graph demonstrating DMC (dimethyl carbonate) selectivity vs. temperature for the MeOH/EC reaction using pseudoboehmite alumina,  $\gamma$ -alumina, and Cs-alumina as the catalysts.

[0016] Figure 3 is a graph demonstrating EG (ethylene glycol) selectivity vs. temperature for the MeOH/EC reaction using pseudoboehmite alumina,  $\gamma$ -alumina, and Cs-alumina as the catalysts.

#### DETAILED DESCRIPTION OF INVENTION

[0017] In accordance with the present invention, a method is provided for the co-production of dialkyl carbonate and alkanediol through the transesterification of alkylene carbonate with alkanol using a IIIA metal oxide catalyst.

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[0018] Generally, all alkylene carbonates can be used as a reactant in this invention. However, low molecular weight alkylene carbonate such as ethylene carbonate, propylene carbonate, butylene carbonate or the like is preferred; ethylene carbonate or propylene carbonate is most preferred.

[0019] Generally, all alkanol reactants can be used, provided the alkanol reacts with cyclocarbonate to produce the dialkyl carbonate and alkanediol product. However, an aliphatic or aromatic alkanol having 1 to 10 carbon atoms is preferably used. For example, methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, secondary butanol, tertiary butanol, allyl alcohol, pentanol, cyclo-hexanol, benzyl alcohol, 2-phenyl ethyl alcohol, 3-phenyl propyl alcohol, 2-methoxy ethanol or the like can be used as the aliphatic or aromatic alcohol. A lower aliphatic alcohol such as methanol is most preferably used due to its reactivity and low cost.

[0020] Further, a phenolic compound can be used in place of the alcoholic compound as the compound which has a hydroxyl (OH) group and reacts with cyclocarbonate to produce the carbonate.

[0021] The catalyst used in the method of the invention is a IIIA metal oxide catalyst. The metal is chosen from the IIIA metals listed on the Periodic Table of elements. Aluminum, gallium, and indium are preferred IIIA metals. Aluminum is most preferred, making alumina the preferred oxide. The catalyst used in the method of the invention will contain only a single metal and, therefore, will not contain a mixed metal oxide. The IIIA metal oxide is the active component and can be supported on any known catalyst support.

[0022] In a preferred embodiment, the catalyst used in the method of the invention contains hydroxyl groups. Hydroxyl group content is defined by the

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weight of hydroxyl group versus the total weight of the catalyst. A large portion of these hydroxyl groups generally reside on the surface of the catalyst. The hydrated catalyst will usually contain hydroxyl groups in an amount greater than 0.1 wt% and less than about 30 wt% of the catalyst; preferably between about 0.3 and 15 wt% of the catalyst. It is believed that the presence of the hydroxyl groups contributes to a higher activity of the catalyst.

[0023] Most of the commercial catalysts of the type used in the method of the invention, such as  $\gamma$ -alumina, have a surface area of about 200-300  $m^2/g$ . A high surface area is preferred in the method of the invention, with no specific upper limit. The catalysts used in the method of the invention typically have a surface area of between about 5-600  $m^2/g$ . A surface area above 50  $m^2/g$  is preferred.

[0024] The IIIA metal oxide catalyst will generally have octahedral or a mixture of octahedral and tetrahedral configuration. Tetrahedral configuration means that the IIIA metal, such as aluminum, is coordinated with four oxygen atoms and forms a tetrahedral geometric structure. Octahedral configuration means that the IIIA metal is coordinated with six oxygen atoms, thereby forming an octahedral structure. Penta-coordinated oxides do exist. However, they are mainly formed during a transition from a octahedral to tetrahedral configuration, such as when an oxide material is being dehydrated. The penta-coordinated configuration is usually present in a relatively small quantity, if at all, in the final IIIA metal oxide catalyst.

[0025] It is preferred that the catalyst used in the method of the invention contain a metal, e.g. aluminum, in octahedral form. Potential catalysts and catalyst precursors that can be utilized in the method of the invention are aluminum trihydroxides such as Gibbsite, Bayerite, and Nordstrandite which can

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be described as a chemical formula,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ; and aluminum mono-hydroxides such as Boehmite, Pseudoboehmite, Diaspore which can be described as a chemical formula,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . These materials are also favored because they contain a high hydroxyl content. Among aluminum mono-hydroxides, Pseudoboehmite (fine boehmite) is desirable for its high surface area and excellent retention of surface area upon calcination. In addition, transient alumina with a high surface area is appropriate for this application, which includes alumina in Gamma, Eta, Delta, Chi, and Theta forms. The nomenclature, structure and transformation of alumina phases have been published by W. H. Gitzen, "Alumina As a Ceramic Material," American Ceramic Society, Inc, Columbus, OH, (1970); J. W. Newsome, et al., "Alumina Properties, Technical Paper No. 10," Alcoa Chemical Company of America, Pittsburgh, PA, (1960), and are incorporated herein by reference.

[0026] The IIIA metal oxide catalyst can also contain alkali metal, alkaline earth metal, or a combination thereof. Alkali metal and alkaline earth metal are both defined to include compounds containing these metals. The specific limits of the amount of alkali and/or alkaline earth metal which can be incorporated into the catalyst can be determined by one skilled in the art, and will vary based upon the specific catalyst and alkali and/or alkaline earth metal used. The amount of alkali and/or alkaline earth metal in the catalyst should not exceed an amount where the pore space of the catalyst is significantly restricted, thereby decreasing the surface area of the catalyst and its activity. For example, if cesium is used as the alkali metal, the amount of cesium will typically be between about 3-50 wt% of the catalyst. Alkali and/or alkaline earth metal may be incorporated into the alumina catalyst by any known means, such as incipient wetness impregnation method.

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[0027] The reactor type in this invention can be any type generally known, such as a continuous fluid bed, fixed bed or stirred tank, etc. With the heterogenous catalyst used in the method of the invention, it is preferred that a fixed bed be used so as to avoid the expense of having to recover the catalyst from the reagents and product.

[0028] The reaction conditions of this invention include a reaction temperature of about 20°C to about 300°C, preferably about 60°C to about 175°C; a reaction pressure of about 14 to about 4000 psig, preferably about 50 to about 400 psig; a liquid hour space velocity of about 0.1 to about 40 hr<sup>-1</sup>, preferably about 0.5 to about 10 hr<sup>-1</sup>; and a molar ratio of alkanol to alkylene carbonate of about 1 to 20, preferably about 2 to 8.

[0029] The following comparative examples are provided to assist in a further understanding of the invention. The particular materials and conditions employed are intended to be further illustrative of the invention and are not limiting upon the reasonable scope thereof.

#### EXAMPLE 1

[0030] This example describes a method for preparing three catalysts employed in the examples.

[0031] Three catalysts employed were: pseudoboehmite (fine particle boehmite) alumina,  $\gamma$ -alumina (prepared from the pseudoboehmite alumina via calcination at 538°C), and Cs-containing alumina. Boehmite is a form of alumina with molecular formula  $(\text{AlO-OH})_n$ . The physical properties of the three alumina samples are shown in Table 1.

TABLE 1

Catalyst	BET Surface Area (m <sup>2</sup> /g)	H Content <sup>a</sup> (millimole/g)	OH, wt% <sup>b</sup>
Pseudoboehmite alumina	356	3.7	6.3
$\gamma$ -alumina	263	1.8	3.1
Cs-alumina	101	1.2	2.0

[0032] The pseudoboehmite alumina, a commercial sample, was pelleted and sized to 80-120 mesh prior to catalyst evaluation.

[0033] The  $\gamma$ -alumina was prepared by mulling the commercial pseudo-boehmite alumina powder with water to form uniform extrudable mixture and formed into 1/8" cylindrical shape extrudates using a standard auger extruder. The extrudates were dried on a belt filter at 250°F (121°C) and calcined under air at 1000°F (538°C) for 3 hours. X-ray powder diffraction showed the phase was converted to the gamma form. The extrudate sample was sized to 80-120 mesh prior to catalyst evaluation.

[0034] The Cs-alumina catalyst was prepared from the above pseudo-boehmite extrudate after drying. Dried alumina extrudates were impregnated with 22% Cs using a solution containing cesium carbonate via incipient wetness impregnation method. The Cs impregnated alumina extrudates were dried at 250°F (121°C) overnight and calcined under air at 1000°F (538°C) for 3 hours. The calcined Cs-alumina sample contained 22.2 wt% Cs and was sized to 80-120 mesh prior to catalyst evaluation.

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## EXAMPLE 2

[0035] This example describes the NMR characterization of the structures and H content of three alumina catalysts; pseudoboehmite,  $\gamma$ -alumina, and Cs-alumina.

[0036] 500.13 MHZ proton MAS NMR spectra were obtained on a Bruker AMX spectrometer using 12-15 kHz sample spinning, 2.7  $\mu$ s pulses, and a 30s recycle time. Chemical shifts are referenced to external TMS at 0.0 ppm. The samples were prepared for proton NMR experiments by drying at 100°C (to remove physisorbed water) under vacuum for 12 hours. An 83.8/16.2 mixture of D<sub>2</sub>O (99% deuterated) and H<sub>2</sub>O was used as the absolute <sup>1</sup>H quantitation standard. The results are summarized in Table 1.

[0037] 130.33 MHZ <sup>27</sup>Al MAS NMR spectra were obtained on a 500 MHZ Bruker AMX spectrometer using 4.0-4.5 kHz sample spinning, 0.8  $\mu$ s excitation pulses, an 80 ms recycle time, and high power proton decoupling. 1M Al(NO<sub>3</sub>)<sub>3</sub> was the external chemical shift reference.

[0038] The pseudoboehmite catalyst is an alumina hydrate containing exclusively octahedral aluminum (surrounded by six oxygen) and high concentration of hydroxyl groups.  $\gamma$ -alumina, on the other hand, contains tetrahedral and penta-coordinated aluminum in addition to octahedral aluminum, and low concentration of hydroxyl groups.

[0039] The <sup>27</sup>Al NMR spectrum of the pseudoboehmite showed a single peak at 5.4 ppm due to octahedral aluminum while three <sup>27</sup>Al resonance peaks at 5.4, 28.0, and 62.1 ppm corresponding to octahedral, penta-coordinated, and tetrahedral aluminum, respectively, were observed for  $\gamma$ -alumina. Cs-alumina

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exhibited two absorptions at 5.4 and 62.1 ppm due to corresponding octahedral and tetrahedral aluminum.

### EXAMPLE 3

[0040] Transesterification evaluations were performed using each of the catalysts described in Example 1.

[0041] The transesterification evaluations were performed in a fixed bed microunit equipped with a three-zone furnace and a down-flow trickle-bed tubular reactor (½" ID). Catalyst powder was pelletized and sized to 80-120 mesh, and the reactor was loaded with 10 cc of the sized catalyst.

[0042] After pressure testing of the unit, the catalyst was dried at 400°F for two hours under 1 atmosphere, 170 cc/min nitrogen flow. At the end of this period, the reactor was cooled down to 150°F (66°C) and nitrogen flow was stopped. The reactor pressure, controlled by a pressure regulator, was then set to 100 psi, and the EC/methanol mixture feed was pumped and added to the top of the reactor at 1.0 h<sup>-1</sup> LHSV. The reactor temperature was gradually increased to initial operating temperature (250°F) (121°C). Each material balance was typically started after the reactor was conditioned for eight hours. Liquid products were condensed in a stainless steel dropout pot at -10°C. Both liquid and off-gas products were analyzed by GC. The catalytic reaction was studied at various temperatures and LHSV to vary EC conversion.

[0043] The three alumina catalysts were evaluated according to the procedures described above. Detailed operating conditions, material balance data, and results on EC conversion and dimethyl carbonate (DMC)/ethylene

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glycol (EG) selectivities for pseudoboehmite alumina,  $\gamma$ -alumina, and Cs-alumina, are summarized in Tables 2, 3, and 4, respectively.

[0044] Feed conversion is calculated based on EC converted during the transesterification reaction since an excessive amount of methanol (relative to EC) was used for all reactions. During EC/MeOH reaction, 2-hydroxyethyl methyl carbonate (HEMC) intermediate was also formed in addition to DMC and EG. The concentration of HEMC varies depending on the reaction conditions. Since it is recyclable along with unreacted EC, the intermediate carbonate is not considered as a byproduct. The feed conversion and product selectivity are defined as follows:

EC Conversion = (EC converted to products other than HEMC)/(total EC in feed)

DMC Selectivity = (moles of DMC formed)/(moles of EC converted to products other than HEMC)

EG Selectivity = (moles of EG formed)/(moles of EC converted to products other than HEMC).

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TABLE 2  
 Transesterification of Ethylene Carbonate with Methanol  
 Catalyzed by Pseudoboehmite Alumina (Condition: 100 psig)

Temperature, °F/°C	250/121	275/135	300/149	325/163	350/177	325/163	325/163	275/135
LHSV, h <sup>-1</sup>	1.0	1.0	1.0	1.0	1.0	4.0	6.0	0.5
<b>Feed Composition</b>								
MeOH/EC, molar ratio	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
<b>Total Liquid Product Composition</b>								
MeOH, wt%	47.8	44.8	43.3	46.5	53.9	46.1	47.5	42.9
EC, wt%	18.8	16.5	14.8	16.2	12.0	18.8	20.2	13.9
HEMC Intermediate, wt%	10.0	7.3	5.9	3.0	1.7	4.9	5.3	6.9
DMC, wt%	15.0	19.1	22.0	19.1	18.4	18.2	16.6	22.6
EG, wt%	10.4	13.3	14.9	11.7	7.2	12.4	11.4	15.6
DMC/EG, Molar Ratio	1.00	0.99	1.02	1.13	1.76	1.01	1.00	1.00
EC Conv., %	36.0	46.4	53.2	55.5	69.1	44.8	40.8	54.0
DMC Selec., %	100.0	98.9	99.1	81.5	60.8	98.1	98.0	99.3
EG Select., %	100.0	99.8	97.3	72.3	34.5	96.8	97.6	99.3

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**TABLE 3**  
**Transesterification of Ethylene Carbonate with Methanol**  
**Catalyzed by  $\gamma$ -Alumina (Condition: 100 psig)**

Temperature, °F/°C	250/121	275/135	300/149	325/163	350/177	325/163	325/135
LHSV, h <sup>-1</sup>	1.0	1.0	1.0	1.0	1.0	4.0	6.0
<b>Feed Composition</b>							
MeOH/EC, molar ratio	4.0	4.0	4.0	4.0	4.0	4.0	4.0
<b>Total Liquid Product Composition</b>							
MeOH, wt%	50.9	49.6	48.0	52.5	57.3	51.0	52.5
EC, wt%	25.1	22.8	19.9	20.7	13.7	23.4	25.7
HEMC Intermediate, wt%	8.8	6.9	3.8	1.6	0.9	2.8	3.1
DMC, wt%	8.7	12.3	16.6	12.2	12.5	12.8	10.5
EG, wt%	6.6	8.3	10.4	5.3	3.3	8.3	7.0
DMC/EG, Molar Ratio	0.91	1.02	1.10	1.59	2.61	1.06	1.04
EC Conv., %	22.8	30.4	43.8	47.4	67.2	35.9	29.4
DMC Selec., %	91.2	99.1	91.9	60.6	41.6	88.0	88.1
EG Select., %	100.0	96.9	83.4	38.1	15.9	82.7	85.1

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**TABLE 4**  
**Transesterification of Ethylene Carbonate with Methanol**  
**Catalyzed by Cs-Alumina (Condition: 100 psig)**

Temperature, °F/°C	250/121	275/135	300/149	325/163	350/177	325/163	325/135
LHSV, h <sup>-1</sup>	1.0	1.0	1.0	1.0	1.0	4.0	6.0
<b>Feed Composition</b>							
MeOH/EC, molar ratio	4.0	4.0	4.0	4.0	4.0	4.0	4.0
<b>Total Liquid Product Composition</b>							
MeOH, wt%	51.5	49.4	46.9	48.2	60.1	51.0	52.1
EC, wt%	24.5	21.8	18.9	18.0	17.4	24.1	25.7
HEMC Intermediate, wt%	9.6	7.0	4.2	2.5	1.0	3.4	3.6
DMC, wt%	8.3	12.8	17.6	17.4	9.0	12.4	10.5
EG, wt%	6.1	8.8	11.5	10.4	2.4	8.2	7.0
DMC/EG, Molar Ratio	0.94	1.00	1.06	1.15	2.59	1.04	1.04
<b>Yield and Selectivity</b>							
EC Conv., %	22.1	32.6	45.8	52.0	58.4	33.9	28.7
DMC Selec., %	90.7	96.1	92.9	79.3	34.6	88.8	90.1
EG Select., %	96.6	95.7	87.9	68.7	13.4	85.1	87.1

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[0045] The comparisons among the three catalysts are made under similar process conditions (feed ratio, pressure, LHSV, etc) and are shown in Figures 1-3. The results demonstrate that a good EC conversion is obtainable with a very high DMC/EG selectivity. Further, the high DMC/EG selectivity is observed over a wider temperature range than for conventional catalysts. An increase in EC conversion is observed with an increase in temperature.

[0046] Table 2 in particular, which relates to the performance of pseudoboehmite, shows that good EC conversion, and  $\geq 98\%$  DMC and EG selectivity are obtainable under optimal reaction conditions. Pseudoboehmite alumina (containing a larger amount of surface hydroxyl groups) exhibits higher activity and DMC/EG selectivity over a wide temperature range vs.  $\gamma$ -alumina and Cs-alumina. Apparently, hydroxyl groups play an important role in promoting the catalytic activity. The observed high selectivity of the hydrated alumina could be due to its low acidity, which inhibits side reactions such as dehydration of alkanols and subsequent hydrolysis of organic carbonates.

[0047] Therefore, the method of the invention is adaptable to commercial application because of the good level of activity, very high selectivity over a wide temperature range, and the stability and relatively low cost of the IIIA metal oxide catalyst used.

[0048] While there have been described what are presently believed to be the preferred embodiments of the invention, those skilled in the art will realize that changes and modifications may be made thereto without departing from the spirit of the invention, and it is intended to claim all such changes and modifications as fall within the true scope of the invention.

**CLAIMS:**

1. A method for co-producing dialkyl carbonate and alkanediol comprising reacting alkylene carbonate with alkanol under process conditions in the presence of a IIIA metal oxide catalyst.
2. The method of Claim 1 wherein said alkylene carbonate is ethylene carbonate and wherein said alkanol is methanol.
3. The method of Claim 1 wherein said IIIA metal oxide is alumina.
4. The method of Claim 3 wherein said alumina is selected from the group consisting of aluminum trihydroxide or aluminum monohydroxide.
5. The method of Claim 4 wherein said aluminum monohydroxide is pseudoboehmite.
6. The method of Claim 1 wherein at least a portion of said IIIA metal oxide catalyst has an octahedral structure.
7. The method of Claim 1 wherein said IIIA metal oxide contains hydroxyl groups.
8. The method of Claim 7 wherein said hydroxyl groups are present in an amount greater than 0.1 wt% and less than 30 wt% of said catalyst.
9. The method of Claim 1 wherein said catalyst further comprises an inert catalyst support.

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10. The method of Claim 1 wherein said process conditions comprise a reaction temperature of about 20°C to about 300°C, a reaction pressure of about 14 to about 4000 psig, a liquid hour space velocity of about 0.1 to about 40 hr<sup>-1</sup>, and a molar ratio of alkanol to alkylene carbonate of about 1-20.

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Ethylene Carbonate (EC) Conversion vs. Temperature  
for the MeOH/EC Reaction Using Pseudoboehmite  
Alumina,  $\gamma$ -Alumina, and Cs-alumina

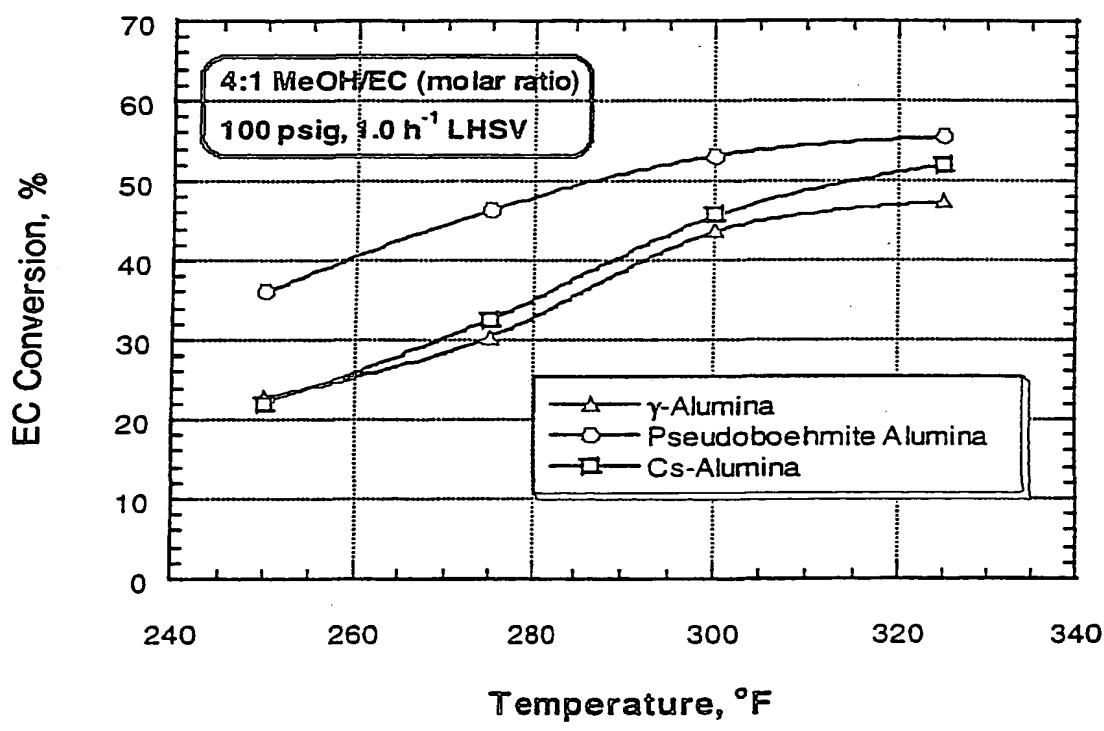


FIG. 1

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Dimethyl Carbonate (DMC) Selectivity vs. Temperature  
for the MeOH/EC Reaction Using Pseudoboehmite  
Alumina,  $\gamma$ -Alumina, and Cs-alumina

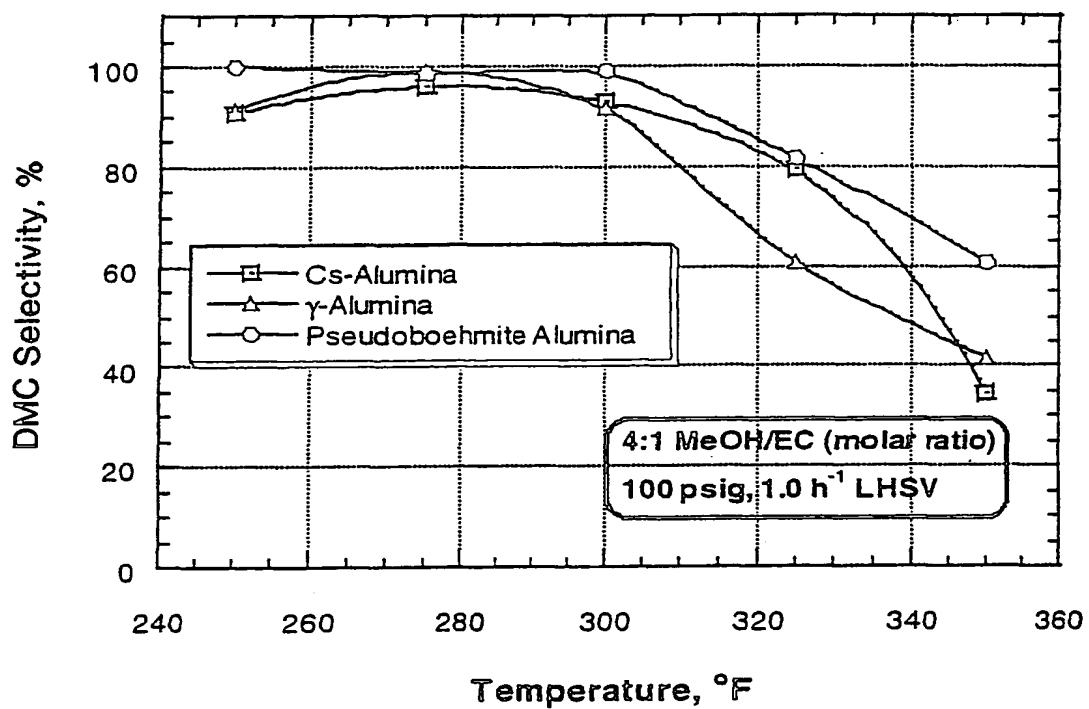


FIG. 2

3/3

Ethylene Glycol (EG) Selectivity vs. Temperature  
for the MeOH/EC Reaction Using Pseudoboehmite  
Alumina,  $\gamma$ -Alumina, and Cs-alumina

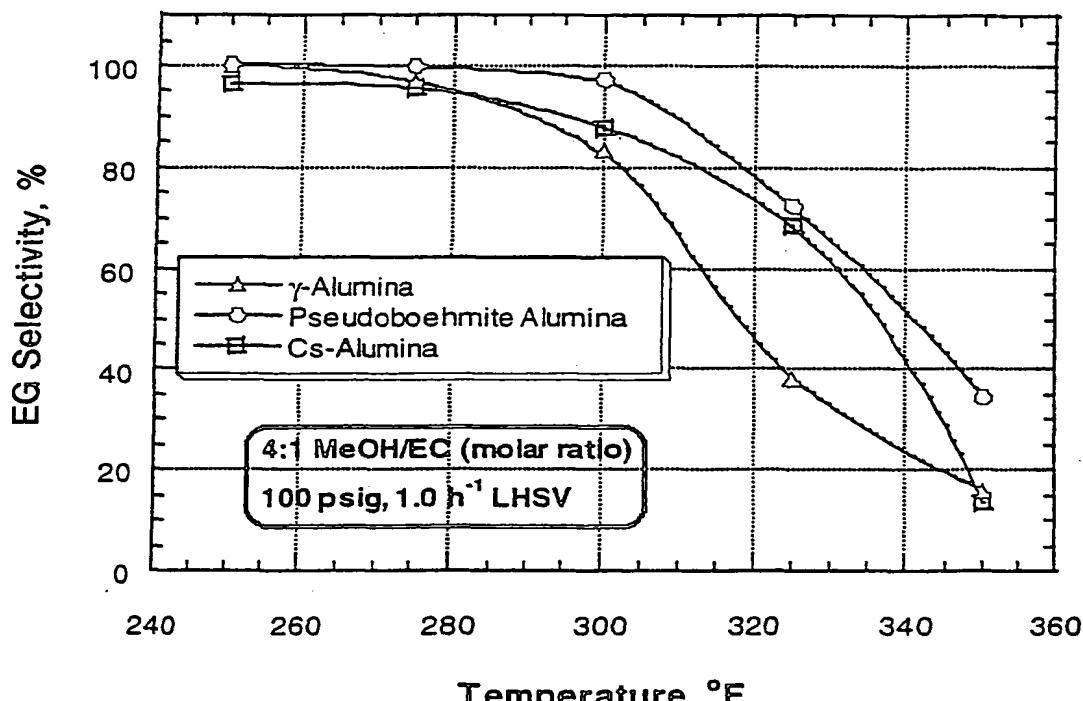


FIG. 3

## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/US 01/07038

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07C68/06 C07C69/96 C07C31/20 C07C27/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 9114 Derwent Publications Ltd., London, GB; Class A60, AN 1991-099158 XP002183057 &amp; JP 03 044354 A (DAICEL CHEM IND), 26 February 1991 (1991-02-26) cited in the application abstract</p> <p>---</p> <p>US 5 430 170 A (Y URANO) 4 June 1995 (1995-06-04) cited in the application examples 5,10</p> <p>---</p>	1-3,10
X		1-3,10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the international search

16 November 2001

Date of mailing of the international search report

28/11/2001

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## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/US 01/07038

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 478 073 A (UNION CARBIDE CHEMICALS AND PLASTICS) 1 April 1992 (1992-04-01) cited in the application examples 3,4,7-20 ----	1-3,10
A	DATABASE WPI Section Ch, Week 9420 Derwent Publications Ltd., London, GB; Class E19, AN 1994-163881 XP002183058 & JP 06 107601 A (NIPPON SHOKUBAI), 19 April 1994 (1994-04-19) cited in the application abstract ----	1
X	US 6 166 240 A (C. D. CHANG) 26 December 2000 (2000-12-26) column 2, line 12 - line 32 ----	1-3,10

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

Int'l Application No	PCT/US 01/07038
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Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 03044354	A	26-02-1991	NONE		
US 5430170	A	04-07-1995	JP 2631803 B2 JP 6211751 A DE 69324331 D1 DE 69324331 T2 EP 0599287 A1 EP 0893428 A1 KR 192771 B1		16-07-1997 02-08-1994 12-05-1999 02-09-1999 01-06-1994 27-01-1999 15-06-1999
EP 478073	A	01-04-1992	CA 2051488 A1 EP 0478073 A2 JP 6025103 A MX 9101179 A1		21-03-1992 01-04-1992 01-02-1994 04-05-1992
JP 06107601	A	19-04-1994	NONE		
US 6166240	A	26-12-2000	NONE		